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(54) PROCESS FOR PRODUCING SUBSTANTIALLY PURE PHENOLS FROM CRUDE PHENOLS OBTAINED BY THE DISSOCIATION OF HYDROPEROXIDES OF ALKYLAROMATIC HYDROCARBONS

(71) We, PHENOLCHEMIE G.M.B.H., a German Body Corporate of, Dechenstrasse 3, Gladbeck, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for the production of substantially pure phenols. The production of phenol by dissociation of cumolhydroperoxide in the presence of acids, is known in principle. The reactive mixture obtained by dissociation is exposed to fractionated distillation, usually following a neutralising action. The initial main distillation product consists of acetone. Isopropylbenzene which may still be present, alphamethylstyrol and water, are obtained as another fraction on further distillation.

The second main top product consists of crude phenol, a mixture of phenol, acetophenone, dimethylphenylcarbinol and *p*-cumylphenol and a series of condensation and polymerisation products, remaining in the sump of the column.

The phenol obtained contains impurities which cause difficulties in processing for the production of different derivatives. These impurities consist mainly of ketones e.g. mesityl oxide, isomesityl oxide, methylisobutylketone, hydroxyacetone and acetophenone. These impurities, and other unidentified impurities, cannot be separated completely from the phenol by distillation, partly because they distil azeotropically with phenol, and partly because they form molecular compounds with phenol.

It is known that phenols obtained by dissociation of cumolhydroperoxide may be purified by heating the gaseous or liquid crude phenol to a temperature of at least 40°C, preferably to a temperature between 100—400° C, in the presence of catalysts having a condensing action, until benzofurans have been formed from the aliphatic alpha-oxycarbonyl compounds present as impurities in the phenol. The phenol is thereafter separated from these benzofurans by extractive distillation in the presence of water. This process is uneconomical, since the water-extractive distillation following the chemical conversion of the impurities is very costly.

In this process, the liquid crude phenol is treated with dissolved iron compounds at a pH value of between 4.5 and 7.5.

According to another known process, the purification of crude phenol is performed by distillation in the presence of auxiliary fluids which preferably have a higher boiling point than the phenol itself. In these conditions, the impurities of the phenol may be drawn off at the top of a primary column and pure phenol may be obtained at the top of the principal column from the residue which contains the auxiliary fluids of higher boiling point, apart from the phenol. Diethylene glycol or diethylene glycolmonobutylether or diethylene glycolether or dipropylene glycol or mixtures of these compounds for example may be employed as auxiliary fluid. This process entails considerable technical complexity and loss of these relatively expensive auxiliary fluids occurs, thereby impairing the profitability of the process as a whole.

A process in which the phenol is treated with inorganic or strong organic acids, proved to be satisfactory in operation. These liquid organic acids, particularly the phenol-sulphonic acids formed by adding concentrated sulphuric acid to the phenol, remain in solution in the phenol. After a neutralising action, they must be removed from the reactive mixture by an additional operation.

The main object of the present invention is to provide a process for the preparation of substantially pure phenols in which the aforesaid disadvantages are minimised.

According to the present invention a pro-

cess for the production of phenols substantially free of ketones, from crude phenols obtained by dissociation of hydroperoxides of alkylaromatic hydrocarbons in the presence of acids, comprises contacting the liquid or vaporous crude phenols at temperatures of between 45°C and 200°C and preferably at temperatures between 80°C and 150°C with fixed bed catalysts consisting of macroreticular ion exchangers and containing active sulphonic acid groups or analogous active acid groups, and distilling the reaction product.

In one embodiment the liquid or vaporous crude phenol is passed over the fixed bed catalyst and the reaction product from the catalyst bed is subsequently distilled to obtain the substantially pure phenol.

Alternatively the crude phenol is distilled in the presence of the fixed bed catalyst under reduced pressures so that substantially pure phenol is distilled off from the reaction product resulting from the action of the catalyst.

These catalysts have been developed as macroreticular ion exchangers. For example, they consist of a base of styroldivinylbenzene copolymer, and of SO_3 representing the active group. These materials are porous and in part possess strongly acid properties, and are employed as a rule in the form of small spheroids.

Macroreticular ion exchangers of this nature are known, for example, under the trade appelations "Amberlyst 15" or "Amberlite 200" or "Lewatit SP 120" and are intended in particular for application in non-aqueous solutions. The words AMBERLYST, AMBERLITE and LEWATIT are Registered Trade Marks. They may also be employed for catalysts of organic reactions in non-aqueous solutions. Their chemical stability in aliphatic and aromatic hydrocarbons and in all other conventional solvents, is extremely high.

The fixed bed catalysts mentioned hereinbefore are technically more appropriate for the purification of crude phenols obtained by dissociation of hydroperoxides of alkylaromatic hydrocarbons in the presence of acids, than concentrated sulphuric acid or strong organic acids such as sulphonic acids. Compared to the application of liquid acids, the application of these fixed bed catalysts has the advantage that they are traversed by the phenol without any appreciable part of this catalyst being entrained by the flow of phenol. A subsequent neutralisation is therefore usually unnecessary. The additional operation such as is required in the case of liquid sulphonic acids, thus also becomes unnecessary.

If small proportions of the fixed bed catalyst are dissolved, thus lowering the pH value below that of the crude phenol, small proportions of substances having an alkaline action are appropriately ducted into this crude phenol to raise the pH value to the initial pH value of the crude phenol. The neutralisation may also be performed by means of anionic exchangers instead of by adding substances having an alkaline action. These exchange resins should obviously be resistant to organic substances such as phenol. In special cases, it may be advantageous to adjust the pH value of the crude phenol to 7 or even more.

The crude phenol is separated by distillation from a residue in the crude phenol column. Apart from impurities already specified, this crude phenol also contains appreciable quantities of alpha-methylstyrene. Substantially all the alpha-methylstyrene is removed at the top from the crude phenol, in a water-extractive distillation. Small proportions of other impurities may concomitantly also be removed from the so-called crude phenol. An "improved" crude phenol remains in the sump of this column, which still contains impurities in the order of 3000 ppm. These impurities, cannot be separated by distillation. If however crude phenols of this kind are ducted in liquid form, at temperatures between 45°C and 200°C and preferably at 80°C—150°C, over such fixedly arranged catalysts, the impurities are converted chemically at the surface of the catalyst. Higher condensation products are usually formed which are separated from the substantially pure phenol by distillation. A small proportion of low boiling point substances are formed and these are separated easily by distillation.

Although it was established that the phenol is preferably ducted over the fixed bed catalyst in liquid form, it was observed that satisfactory efficiency is also secured if the phenol flows over the fixed bed catalyst in gaseous form. This operation is preferably performed under reduced pressure.

The purifying action of such fixed bed catalysts depends in particular on the temperature and dwell period of the liquid phenol. The efficiency is lower at lower temperatures than at higher temperatures. The purifying action may be varied by varying the dwell period of the liquid phenol, i.e. by varying the velocity of flow. Optimum purifying actions may be obtained, simultaneously affecting the durability of the catalyst, by combining an average dwell period with an average temperature. The preferred temperatures lie between 80°C and 150°C, the dwell periods of the crude phenol on the catalyst being varied between 5 and 60 minutes. At higher temperatures, e.g. 180°C, the dwell period on the catalyst may be shortened considerably so that dwell periods of less than 1 minute are possible. On the other hand, dwell periods exceeding 1 hour may be necessary to ensure the required purifying action.

According to the invention, it is possible to operate in such manner that the liquid or vaporous phenol is ducted over only one of these fixed bed catalysts in each instance. It is also possible however to employ these cata-

lysts in combination, for example initially ducting the crude phenol over an "Amberlite" as a fixed bed catalyst, and then complementarily over an "Amberlyst" as a fixed bed catalyst. Combinations of other fixed bed catalysts may also be employed. Specific advantages may accrue therefrom for the purifying action as a whole, because the effectiveness of the different catalysts is of partially different nature. The purification of the crude phenol may however also be conducted in such manner as to perform a preliminary purification in the presence of small quantities of liquid acids, prior to ducting this preprocessed crude phenol over the fixedly arranged catalysts. The quantities of acid employed for this purpose amount to less than 0.05 % by weight. Normally, quantities of acid in liquid form of approximately 0.01 % by weight and less are adequate for a combined procedure of this kind.

The purification of the crude phenol may also be performed in such manner that the crude phenols are ducted initially over one or more fixed bed catalysts, and are then processed complementarily with liquid acids in quantities of less than 0.05% and preferably of less than 0.01%.

As mentioned hereinbefore, the temperature of reaction plays an important part anent the effectiveness of the catalysts. Different temperatures may be applied to obtain optimum efficiency when employing a combination of catalysts. This means that the crude phenol may be at a different temperature during preliminary treatment with small quantities of liquid acids, from that applied during subsequent ducting over a fixed bed catalyst. The temperatures will be chosen to obtain optimum purifying actions.

The reaction product obtained from the catalyst bed, is refined into pure phenol in conventional manner, the volatile substances being removed in a primary pure phenol column, the substantially pure phenol itself then being distilled off at the top of the pure phenol column. The products of higher boiling point formed during the catalytic action of the fixed bed catalysts on the impurities of the crude phenol, remain in the sump of this pure phenol column.

The process of the invention may be applied not only during the purification of phenol obtained by dissociation of isopropylbenzenehydroperoxide, but may also be applied in the same manner in the case of phenols obtained during the dissociation of hydroperoxides of other alkylaromatic hydrocarbons, e.g. di-isopropylbenzene, methylisopropylbenzene or isopropylnaphthalene.

The invention will now be further described with reference to the following Examples.

Example 1

1 kg of a crude phenol obtained by dissociation of isopropylbenzolhydroperoxide in the presence of acid, freed of impurities of lower boiling point than phenol by distillation and which thereafter still contained approximately 2800 mg of ketones, calculated in the form of mesityl oxide, and a small quantity of other impurities, was ducted over a fixed bed catalyst consisting of the already defined product having the trade name Amberlyst 15. The reaction temperature being 120°C and the dwell period of the phenol on the fixed bed catalyst being approximately 60 minutes. After leaving the fixed bed catalyst, the phenol was neutralised with a small quantity of powdered sodium carbonate, and was then distilled. Runnings of approximately 5% were drawn off initially, after which phenol was obtained until the end of the distillation, possessing very good solubility and having a total ketone content of less than 10 mg/kg, calculated as mesityl oxide. This phenol complies with the purity requirements prescribed for the special purposes specified.

Example 2

1 kg of crude phenol obtained in the manner described in Example 1, still containing approximately 3300 mg of ketones calculated as mesityl oxide and a small quantity of other impurities, was ducted over a fixed bed catalyst consisting of the product having the trade name Amberlite 200 at a temperature of 145°C. The dwell period of the phenol on the fixed bed catalyst was approximately 15 minutes. After neutralisation with aqueous soda lye, the reaction product was fractionally distilled. After drawing off first runnings of 5%, a phenol was obtained which contained approximately 100 mg/kg of ketones calculated as mesityl oxide.

Example 3

1 kg of crude phenol obtained in the manner described in Example 1 and still containing approximately 2200 mg of ketones calculated as mesityl oxide and other impurities, was processed with concentrated sulphuric acid in a quantity of 0.01%, for 2 hours, at a temperature of 120°C. This crude phenol was then ducted over a fixed bed catalyst consisting of Amberlyst 15. After a dwell period of approximately 5 minutes, the acid crude phenol leaving the fixed bed catalyst was neutralised with aqueous soda lye. After drawing off first running of 5%, a pure phenol was obtained. which contained approximately 50 mg/kg of ketones calculated as mesityl oxide.

Example 4

1 kg of crude phenol obtained in the manner described in Example 1 and still containing approximately 3000 mg of ketones calculated as mesityl oxide. and other impurities, was ducted over a fixed bed catalyst consisting of Amberlite 200 at a temperature of 130°C.

The dwell period of the crude phenol on the fixed bed catalyst amounted to 10 minutes. This crude phenol was then treated at the same temperature with 0.01% of concentrated sulphuric acid. After 2 hours, neutralisation was performed with solid sodium carbonate. After drawing off first runnings of less than 5%, a pure phenol was obtained which contained less than 50 mg of ketone per kg, calculated as mesityl oxide.

EXAMPLE 5

1 kg of crude phenol obtained in the manner described in Example 1 and which still contained approximately 2500 mg of ketones calculated as mesityl oxide and other impurities, was distilled at approximately 100 Torr in a lined column 50 cms high and equipped with a vacuum casing, filled with a mixture of Braunschweig coils and Amberlyst 15. After drawing off first runnings of approximately 5%, a pure phenol was obtained, which contained less than 100 mg of ketones per kg, calculated as mesityl oxide.

WHAT WE CLAIM IS:—

1. A process for the production of phenols substantially free of ketones, from crude phenols obtained by dissociation of hydroperoxides of alkylaromatic hydrocarbons in the presence of acids, comprising contacting the liquid or vaporous crude phenols at temperatures of between 45°C and 200°C with a fixed bed catalyst consisting of macroreticular ion exchangers and containing active sulphonic acid groups or analogous active acid groups, and distilling the reaction product.

2. A process according to Claim 1, wherein liquid or vaporous crude phenol is passed over the fixed bed catalyst and the reaction product from the catalyst bed is subsequently distilled to obtain the substantially pure phenol.

3. A process according to Claim 1, wherein the crude phenol is distilled in the presence of the fixed bed catalyst under reduced pressure, so that substantially pure phenol is distilled off from the reaction product resulting from the action of the catalyst.

4. A process according to any of Claims 1 to 3, wherein the liquid or vaporous crude phenols are contacted with the fixed catalyst bed at a temperature of between 80°C and 150°C.

5. A process according to any of Claims 1 to 4, wherein the crude phenol is treated with liquid acids, preferably with sulphuric acid, in quantities of less than 0.05% by weight, before or after its processing with fixed bed catalysts.

6. A process according to any of Claims 1, 2, 4 or 5, wherein the reaction product is neutralised before performing the distillation.

7. A process of preparing substantially pure phenols substantially as herein described with reference to any of Examples 1 to 5.

8. Substantially pure phenol whenever prepared by the process of any of Claims 1 to 7.

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